HIGH TEMPERATURE H_2S REMOVAL
FROM PROCESS GASES IN A STEAM REGENERATIVE PROCESS
USING MnO OR FeO ON γ-ALUMINA ACCEPTORS

J.P. Wakker, A.W. Gerritsen
Delft University of Technology,
Laboratory of Chemical Process Technology,
Julianalaan 136, 2628 BL Delft, The Netherlands.

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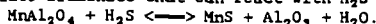
Abstract

During gasification of coal the sulfur compounds are converted mainly into H_2S and COS. A process to remove these compounds at temperatures of 400-800 °C has been developed. The acceptors used are based on MnO or FeO on a γ-alumina carrier. Regeneration takes place at the same temperature with a gas containing steam, while more than 15 %v of H_2S can be obtained in the dried reactor off gas. The main advantage of steam regeneration is that no oxidation or noticeable heat effect is involved. A packed bed microreactor was used to study sulfidation- and regeneration behaviour extensively in cyclic experiments. It showed that H_2S can be removed to a level of 0-50 ppmv depending upon gas composition. After several hundreds of cycles only little deactivation was observed. The effects of various compounds in the feed were studied.

Introduction

Thermodynamics of the reaction $MnO + H_2S \longleftrightarrow MnS + H_2O$ in the temperature range 400-800 °C indicate that the equilibrium is shifted completely towards the metal sulfide. This means that MnO can remove H_2S at these temperatures quite deep but also that steam will not regenerate a sulfur loaded acceptor. Consequently it may sound strange that a MnO on γ-Al_2O_3 acceptor is proposed here! However, fact is that such an acceptor can remove H_2S effectively at 400-800 °C and is regenerated easily with steam at the same temperature [1, 2].

Other H_2S acceptors often use air for regeneration, resulting in sulfur oxides as well as an oxidized accepter, both needing a reducing agent like H_2 to obtain acceptable products. The heat produced may result in temperature control problems and sintering of the acceptor material. In contrast the MnO on γ-Al_2O_3 acceptor is regenerated without a noticeable heat effect, resulting in a stable acceptor. As regeneration does not change the oxidation state of the acceptor, no reduction is needed either. The H_2S formed can be used directly to generate sulfur, e.g. in a Claus plant. This ability to regenerate MnO on γ-Al_2O_3 acceptors with steam is not incidental, on the contrary: -after a relative short stabilization time- the acceptors can be exposed to more than 400 sulfidation-regeneration cycles without a change in activity .

At Delft University of Technology (DUT) several investigations were performed to determine which compound(s) are responsible for the fact that steam regeneration is possible [3]. It is supposed that regenerable acceptors are formed from a monolayer of MnO which reacted with the γ-alumina carrier and produced a surface aluminate. In other words: free MnO on Al_2O_3 is expected to be non-regenerable, while MnO with a crystalline structure close enough to that of the γ-Al_2O_3 carrier will form a surface-aluminate that can react with H_2S according to:
$$MnAl_2O_4 + H_2S \longleftrightarrow MnS + Al_2O_3 + H_2O.$$
The equilibrium constant of this reaction can be estimated and compared with that of pure manganese oxide. In figures 1a and 1b are shown, respectively, the thermodynamic equilibrium constant for FeO and MnO, in contact with a H_2S-H_2O gas mixture and the reaction enthalpies for the sulfidation. For the pure metal oxides the sulfidation equilibrium is shifted completely towards the metal sulfide at temperatures from 400 to 800 °C. As can be seen from figure 1a the thermodynamic constants of the corresponding aluminates $MnAl_2O_4$ and $FeAl_2O_4$ indicate that their equilibrium with a H_2S-H_2O gas mixture is not pronounced to one side. In these

figures both Fe and Mn oxides are shown because it was found that not only MnO on γ-Al$_2$O$_3$ can be used in a steam regenerative process to remove H$_2$S. Quite similar behaviour is found with FeO on γ-Al$_2$O$_3$, the same holds even for Zn, Ni and Co. However, only FeO on γ-alumina comes close to MnO on γ-alumina, the others are far less attractive.

Several investigations support that an aluminate is the active substance.
Atomic absorption measurements in combination with sulfidation-regeneration experiments of acceptors with different metal oxide levels show that, up to a certain coverage, all metal sulfide formed can be regenerated with steam. That coverage corresponds to a number of metal oxide moles equal to the number of alumina moles exposed at its surface.
Although the assumption that manganese aluminate is the active compound could not be confirmed by röntgen diffraction, this technique did not prove the opposite either. No lines characteristic for this compound could be found, probably due to its high dispersion on a carrier of poor crystallinity. Irregenerable acceptors however show lines that correspond with those of pure MnO.
Diffuse reflectance spectroscopy at reaction conditions shows that regenerable acceptors have bands characteristic for MnAl$_2$O$_4$ (as indicated by their grey colour) while irregenerable acceptors have a MnO spectrum (and a brown colour).
Another technique used is Mössbauer spectroscopy, although it could only be applied to iron oxides as manganese has no Mössbauer activity. From this study it can be concluded that on steam-regenerative acceptors the Fe^{2+} ions are highly dispersed on the support and built-in into the alumina. This agrees with the formation of FeAl$_2$O$_4$.

Experimental
Acceptor preperation
Using the wet impregnation technique the carrier is contacted with a solution of a metal salt at ambient temperature. After approximately 16 h the impregnated material is filtrated and dried, generally overnight, at about 110 °C. In some cases, e.g. in case a metal acetate or -oxalate was used, the drying was combined with calcination at 300 °C. Finally the material, with the metal still in a high oxidation state (e.g. MnO$_2$), is reduced with H$_2$ at 600 °C. Depending on the metal content desired the complete process is repeated a number of times.

Table 1 shows that the number of preparation cycles and the molarity of the salt solution not only determine the amount of manganese obtained on the carrier, but also whether or not such an acceptor can be regenerated completely. Although not indicated in the table, with each salt it is possible to obtain an acceptor which can not be regenerated completely. This is done by raising the manganese content above 8-10 %w. Notably this agrees with a 1:1 mole ratio of metal to surface alumina.

Instrumental

The apparatus used to obtain the sulfidation-regeneration data is described schematically in figure 2. The heart of the apparatus is a tubular quartz reactor with an internal diameter of 9 mm. Normally 3 g acceptor, with a mean particle diameter of 0.4 mm, result in a bed length of approximately 70 mm. The reactor is kept at a constant temperature, which can be choosen between 400 and 800 °C. The reactor is used in a cyclic way: about 1.5 hour it is used to remove H$_2$S from the gas stream fed (the sulfidation- or acceptation phase), then for about half an hour the sulfur is removed from the acceptor (the regeneration phase). The cycle is completed with a flush phase of another half hour.
In the acceptation phase the feed to the reactor is obtained by mixing gases from cylinders. Generally the H$_2$S content is 1 %v and the hydrogen content 10 %v, the balance being N$_2$. The total flow rate is 100 ml/min at ambient conditions. Several other gases, notably CO and CO$_2$ can be added as well. If the influence of small amounts of H$_2$O is studied, the feed is passed through a bed of FeSO$_4$.7aq. This results in a H$_2$O content of 0-5 %v, depending upon the temperature of the FeSO$_4$

bed. If the H_2O concentration has to be higher than 5 %v, liquid water is injected into the reactor. This will evaporate before reaching the acceptor bed.
Quite different amounts of water are needed during regeneration. In this phase the H_2S supply is closed and a small stream of water injected, resulting in a flow with approximately 50-80 %v of steam.
The H_2S content in the outlet is monitored by passing the gas through a stirred vessel with a $CdSO_4$ solution, kept at a constant pH of 4 by introducing NaOH as well. Under above conditions the flow of NaOH supplied equals the flow of H_2S leaving the reactor. The concentration of H_2S can be obtained as the first derivative of this flow towards time. Other compounds (CO, COS, CO_2, H_2S and H_2O) in the reactor effluent can be detected with a gas chromatograph. In this way e.g. the shift-reaction can be followed.

A typical breakthrough curve, which describes the outlet H_2S concentration during the acceptation phase, is shown in figure 3. At the start of an experiment all H_2S supplied is captured by the acceptor. After approximately 20 minutes a sudden increase of the H_2S concentration indicates breakthrough. Within a few minutes thisconcentration raises to about 30-40% of the inlet value. Of course in practice breakthrough will never be waited for. Some time before this moment is expected, another reactor with fresh or regenerated acceptor will be used. During our investigations the outlet concentration is monitored for about 1 h more because the complete curve gives valuable information about the concentration profile within the acceptor bed in the time-span BEFORE actual breakthrough.
After enough data are gathered the H_2S supply is switched off and steam introduced. Now H_2S is being produced. Again the H_2S content is monitored as a function of time to obtain kinetic data. This proceeds until all sulfur captured during acceptation has been released.

Results and discussion
An interesting variable is the amount of sulfur captured at breakthrough (qb) as a function of the time on stream. As can be observed in figure 4 a fresh acceptor will take up some 2 % of its weight as sulfur at 600 °C. This decreases gradually to approximately 1 % in the first week and remains constant at that level afterwards, at least until some 80 days, or approximately 400 cycles, later. This deactivation can, to a certain extent, be explained by the decrease in surface area which was determined in parallel to this experiment. The corresponding BET surfaces are shown in the figure. It should be noted here that the temperature was kept at 600 °C all the time. At this temperature the deactivation will also take place if the acceptor is NOT subjected to acceptation-regeneration cycles but left in a reducing atmosphere only. If a fresh acceptor is used and the temperature maintained at 400 °C, no or little deactivation takes place. At 800 °C the acceptor will take up 2.7 %w S, but this capacity decreases in about five weeks to approximately 1 %w S, probably due to sintering of the carrier material.

The influence of temperature on a "stabilized acceptor" is shown in figure 5. Lowering the temperature from 600 °C to 400 °C results in a decrease of sulfur capture at breakthrough by approximately one half. When the acceptors are stabilized at 800 °C instead of 600 °C lowering the temperature from 800 °C to 600 °C results in a decrease of the breakthrough capacity from 2.7 %w sulfur to approximately 0.5 %w sulfur. The same behaviour is observed for iron containing acceptors. This decrease is attributed to both kinetics and thermodynamics.

The influence of the H_2S concentration itself on the breakthrough capacity is given in figure 6. At low H_2S concentrations the capacity is somewhat higher than at high concentrations. This can be explained by summation of two processes. The first process is a fast equilibrium between H_2S and surface aluminate; the corresponding acceptor capacity is not influenced by the H_2S concentration. The second process is slow and corresponds to sulfur that moves to sites that are not easily reached. This means that when low H_2S concentrations are used (while the volumetric flow rate is kept constant) the second, relatively slow process can proceed longer before breakthrough is measured, resulting in a higher capacity.

In all experiments hydrogen is added to the feed to prevent decomposition of H_2S into hydrogen and sulfur. As long as the feed gas only contains N_2, H_2 and H_2S the H_2 concentration does not influence the reaction rate in the range of 7 to 90 %v.
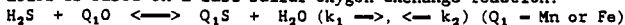
The results discussed so far are obtained with a feed of 1 %v H_2S, 10 %v H_2, the balance being N_2. In general, however, the feed will contain CO, CO_2 and H_2O as well. As could be expected from the possibility to use steam as the regenerative agent, H_2O has a negative effect on the amount of sulfur captured at breakthrough. This is demonstrated in figure 7a. In this figure the relative breakthrough capacity is shown as a function of the water content of the feed. The relative breakthrough capacity is the observed breakthrough capacity divided by the breakthrough capacity of the same acceptor using a standard feed gas without water. In this way the capacities of different acceptors can be compared easily. The retention level decreases drastically by 15 %v of H_2O. However, CO in the feed has a positive effect on the sulfur retention capacity as is demonstrated in figure 7b, which shows that 50 %v CO will increase that capacity by a factor of approximately 1.4 for the manganese acceptor and a factor 1.7 for the iron containing acceptor. From this figure the influence of the hydrogen concentration can be seen clearly too. The positive effect of 50 %v CO is a factor 1.9 if the feed gas contains only 10 %v hydrogen instead of 40 %v hydrogen. A combination of both effects, the negative water influence and the positive CO influence, can be observed in figures 8a and b.

The effect of CO can be explained by the shift reaction: $CO + H_2O \longleftrightarrow CO_2 + H_2$. Both the water fed to the reactor and the water produced in the reaction of H_2S with the acceptor react with CO to form a CO_2/H_2 mixture.
Another effect of introducing CO is the formation of COS by the analogous equilibrium: $CO + H_2S \longleftrightarrow COS + H_2$. Fortunately it showed that COS only appears in the effluent after H_2S breakthrough, indicating that COS is effectively removed by the acceptor as well. The COS formation is quite fast, the COS in the gas leaving the reactor is almost in equilibrium with the other gas constituents.
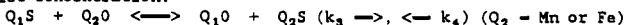
Other compounds which may be found in practical feedstocks are hydrocarbons as CH_4, C_2H_6 and lower alkenes. Experiments showed that these compounds have no influence on acceptor behaviour if their content is lower than 10 %v. Even higher levels are allowed, although some influence may start to be visible, especially in case of alkenes.

Recently the regeneration of the acceptors has been studied in more detail [4]. Figure 9 shows the amount of steam needed to regenerate acceptors which were previously completely loaded with sulfur. By dividing this amount by the amount needed stoechiometrically, the relative steam use RSU is obtained. It can be seen that two-third of the sulfur captured can be regenerated easily, the rest needs a higher amount of steam. Similar figures are available for different steam concentrations, all indicating that a high steam concentration and a low steam space velocity is best. The resulting off gas may contain up to 25 %v of H_2S on wet basis or 40 %v or more on dry basis. Such a gas can be used quite well in a Claus unit.

Another part of the study is focussed on a mathematic model to decribe the results. The model is based on a fast sulfur-oxygen exchange reaction:
$$H_2S + Q_1O \longleftrightarrow Q_1S + H_2O \ (k_1 \longrightarrow, \longleftarrow k_2) \ (Q_1 = Mn \text{ or } Fe)$$
A slow sulfur-oxygen exchange reaction is added to explain the slow rise of the outlet concentration:
$$Q_1S + Q_2O \longleftrightarrow Q_1O + Q_2S \ (k_3 \longrightarrow, \longleftarrow k_4) \ (Q_2 = Mn \text{ or } Fe)$$
Next "Langmuir" adsorptions are needed to account for the amount of H_2S that can be desorbed from a loaded acceptor without using any steam; it is assumed that the same sites also adsorb H_2O:

$$H_2S + Q_3 \longleftrightarrow Q_3\text{-}H_2S \qquad\qquad (Q_3 = Al_2O_3)$$
$$H_2O + Q_3 \longleftrightarrow Q_3\text{-}H_2O \qquad\qquad (Q_3 = Al_2O_3)$$

Mathematically this set of equilibria is difficult to solve, mainly because the H_2S and H_2O concentrations are independant. In practice 4 stiff partial differential equations have to be solved simultaneously.

Results obtained with this model are given in figures 10a and b. With the model a good fit is obtained. The fact that the calculated H_2O outlet curve is not in agreement with the experimentally found curve is not taken too serious because the H_2O analysis was much less reliable.
The parameters used to obtain these curves are summarized in table 2. Of course much work is still to be done in this field, e.g. we are to determine some of the parameters of the last table by independent other techniques like thermogravimetrics, and the effect of CO has to be incorporated in the model.

Also in the field of practical experiments progress is made. In the near future the acceptors will be tested in a larger unit to desulfurize a sub-stream of gas leaving the experimental 200 kW (thermal) gasifier build at the Energy Research Centre of the Netherlands in Petten. The unit consists of 3 reactors (1.5 liter volume each) which are used intermittently. While one is in the acceptation phase the acceptor in one of the others is regenerated. This work is described extensively in next paper presented at this congres.

Conclusions
The acceptors developed at DUT can remove H_2S from a fuel gas and can be regenerated with a gas containing steam. This behaviour can be explained by the formation of a surface $MeAl_2O_4$ (Me = Mn or Fe) spinel.
The amount of sulfur captured at breakthrough varies between 0.25 and 3.0 %w, depending upon temperature and gas composition. The regeneration off-gas contains up to 40 %v H_2S, enough to be fed to a Claus plant. The acceptors have a long lifetime: they can be used during at least 400 sulfidation-regeneration cycli.

SYMBOLS USED:

BET	B.E.T. surface area of acceptor	[m^2/g]
C_i	outlet concentration of component i	[%v]
C_i^i, feed	inlet concentration of component i	[%v]
dp	particle diameter of acceptor	[mm]
ΔH	reaction enthalpy sulfidation reaction	[kJ/mol]
K	equilibrium constant sulfidation reaction	[-]
K_{H_2O}	equilibrium constant H_2O adsorption Langmuir sites	[m^3/mol]
K_{H_2S}	equilibrium constant H_2S adsorption on Langmuir sites	[m^3/mol]
k_1, k_2	rate constants fast exchange reaction	[m^3/(mol.s)]
k_3, k_4	rate constants slow exchange reaction ($k_3 = k_4$)	[m^3/(mol.s)]
L	length acceptor bed	[mm]
q_b	breakthrough capacity, sulfur captured at breakthrough	[%w]
$q_{b,rel}$	relative breakthrough capacity = observed breakthrough capacity divided by the breakthrough capacity of the same acceptor using standard feed gas	[-]
Q_{theor}	theoretical maximal capacity of acceptor	[mol/m^3]
Q_1	stoechiometric capacity of fast exchange sites	[mol/m^3]
Q_2	stoechiometric capacity of slow exchange sites	[mol/m^3]
Q_3	stoechiometric capacity of Langmuir sites	[mol/m^3]
T	temperature	[°C or K]
θ	H_2S throughput parameter = amount of sulfur fed during acceptation divided by an arbitrary amount of sulfur	[-]
#	number of impregnation cycles	[-]

Literature:
[1] J. Barin, O. Knacke, O. Kubachewski, "Thermochemical Properties of Inorganic Substances", Springer Verlag, Berlin, 1973, Supplement, 1976.

[2] D.R. Stull, H. Prophet, "JANAF Thermochemical Tables", 2nd ed., National Bureau of Standards, Washington D.C., 1971.
[3] T.H. Soerawidjaja, "Steam regenerative removal of H_2S at high temperatures using metal oxide on alumina acceptors", Thesis, Delft University Press, 1985.
[4] R. van der Heijden, A.W. Gerritsen, I^2-Procestechnologie, 10, 11-18 (1987).

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Table 1. Influence of salt, molarity and number of impregnations on ability to be regenerated by steam.

Salt	#	mol	Mn %w	Regeneration %
Nitrate	1 x	2.0	7.9	69
	4 x	0.7	10.1	95
	4 x	0.5	8.0	100
Sulfate	3 x	0.5	7.2	100
Acetate	1 x	2.0	7.7	100

Table 2. Parameters of the model at 400 and 600 °C

Param	Dimension	400 °C	600 °C
k_1/k_2	-	4.7	3.6
k_1	$m^3/(mol.s)$	0.4	0.4
Q_1	mol/m^3	160	209
k_3-k_4	$m^3/(mol.s)$	1E-3	7E-7
Q_2	mol/m^3	140	210
K_{H_2S}	m^3/mol	1.38	1.36
K_{H_2O}	m^3/mol	14.7	12.4
Q_3	mol/m^3	140	168

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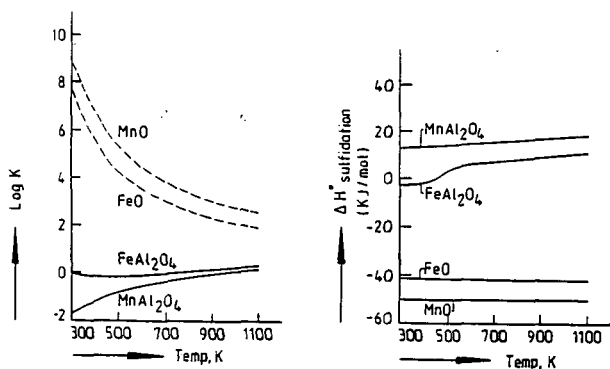
Figure 1: Thermodynamic data of sulfidation.
a: Equilibrium constant.
b: Heat of reaction.
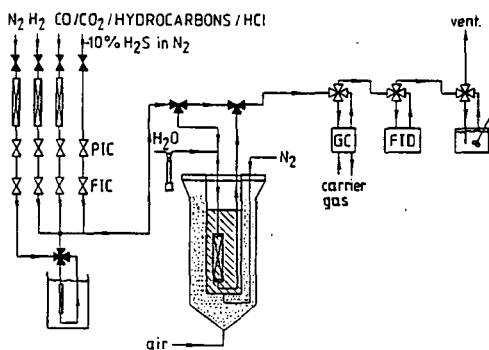
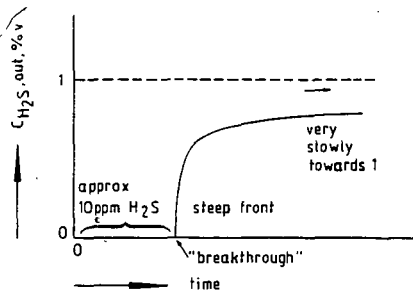Figure 2: Apparatus used for sulfidation-regeneration experiments.

Figure 3: Typical H_2S breakthrough- or elution curve.
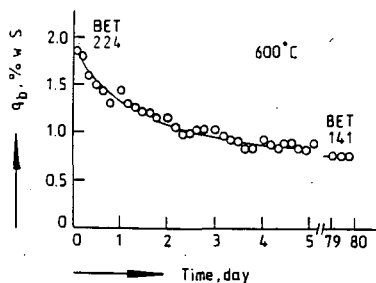Response of $C_{H_2S,out}$ on stepwise increase of $C_{H_2S,in}$ at time = 0.

Figure 4: Stabilization of acceptor at 600 °C.
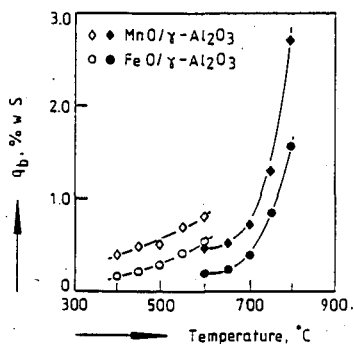Sulfur captured at breakthrough as a function of time.

Figure 5: Influence of temperature on breakthrough capacity.
Acceptors: 8.1 %w Mn on γ-alumina (open diamond)
8.2 %w Mn on γ-alumina (solid diamond)
4.5 %w Fe on γ-alumina (open circle)
4.6 %w Fe on γ-alumina (solid circle)
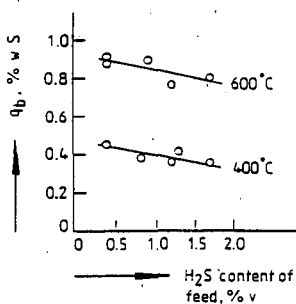
Figure 6: Influence of H_2S content of feed on
breakthrough capacity.
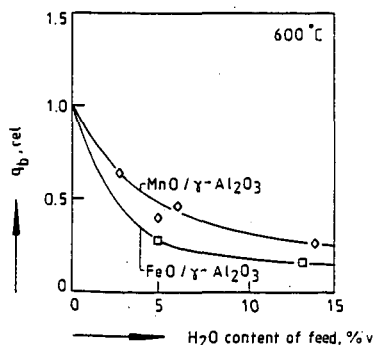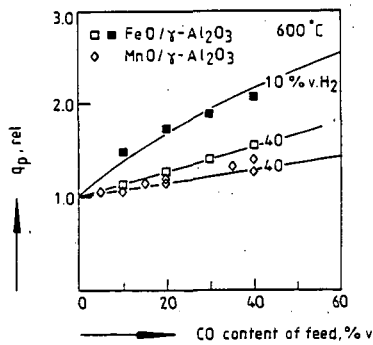Acceptor: 8.1 %w Mn on γ-alumina.
Temperature: 400 and 600 °C.

Figure 7: Influence of H_2O content, CO and H_2 content of feed on breakthrough capacity. Temperature: 600 °C.
Acceptor: 8.1 %w Mn on γ-alumina
4.6 %w Fe on γ-alumina.
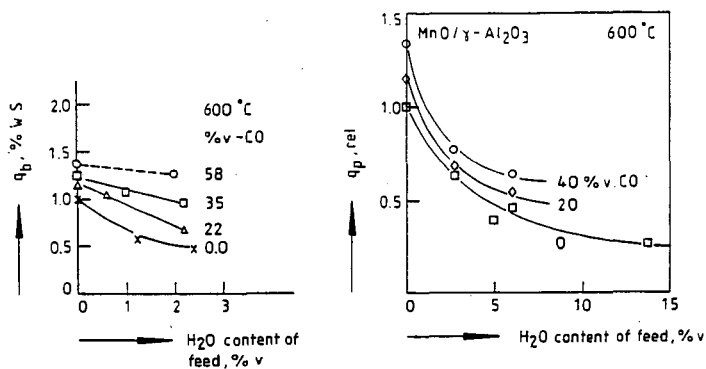a: Influence of H_2O content   b: Influence of CO and H_2 content

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Figure 8: Combined influence of H_2O and CO in feed on breakthrough capacity. Acceptor: 8.1 %w Mn on γ-alumina. Temperature: 600 °C.
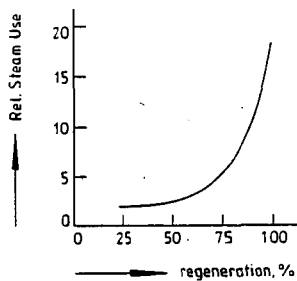a: 10 %w H_2 b: 40 %w H_2

Figure 9: Relative Steam Use (RSU) as a function of percentage of acceptor that is regenerated. RSU is the amount of steam supplied during generation, divided by the amount needed stoechiometrically for complete regeneration.
Acceptor: 8.1 %w Mn on γ-alumina. Temperature: 600 °C.
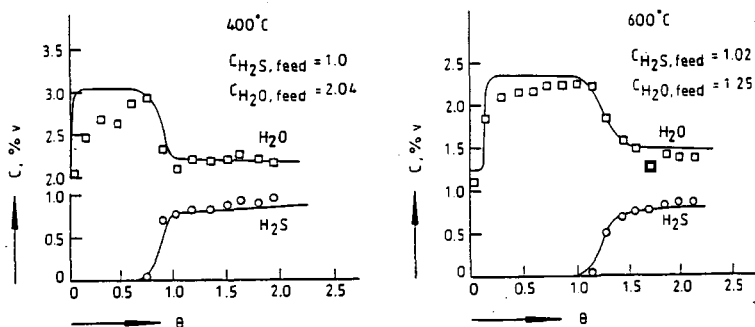

Figure 10: Comparison of experimental and simulated breakthrough curves.
a: Temperature 400 °C.   b: Temperature 600 °C.

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